

Preparation and Properties of Fibers from a Crystalline Polymethacrylonitrile

MASAHIKO MIYANOKI and YASUSHI JOH,* *Research Laboratories, Mitsubishi Rayon Co., Ltd., Hiroshima 739-06, Japan*

Synopsis

Fibers from a crystalline polymethacrylonitrile were prepared by dry spinning using trifluoroacetic acid as solvent. Stretchability increased when the solvent retained in the fiber was extracted with methanol. Tensile properties are well acceptable for practical use. It is notable that the stress-strain curve for the polymethacrylonitrile (PMAN) fiber shows clear yield point even under hot-wet condition (90°C in water). Thus, the PMAN fiber is expected to have improved "hot-wet properties" compared with conventional acrylic fibers. From the data in the compliance and resiliency maps, the PMAN fiber is expected to be one of the most promising fibers having wool-like properties.

INTRODUCTION

A rapid development in the field of polymer chemistry has brought us innumerable new polymers in recent years. A crystalline polymethacrylonitrile having an isotactic structure has been successfully synthesized by Natta et al.¹ and Joh et al.²⁻¹³ However, there has been no report on the practical utilization of this new polymer so far. The present paper deals with the preparation and characterization of fibers made from a crystalline polymethacrylonitrile. Fibers were prepared by dry spinning using trifluoroacetic acid as solvent. The fibers obtained have good tensile properties and are expected to be more wool-like than conventional acrylic fibers.

EXPERIMENTAL

Polymer Preparation

Isotactic polymethacrylonitrile (PMAN) was prepared in toluene with diethylmagnesium. The details of the polymerization were reported in other papers.^{2,3,7}

The dimethylformamide-insoluble, crystalline part (intrinsic viscosity, 1.5 dl/g in Cl₂CHCOOH at 30°C, $M_w = 112,000$) was used for the preparation of fiber.

For comparison, a copolymer consisting of 93% acrylonitrile and 7% vinyl

* Present address: Nippon Zeon Co., Ltd., Furukawa Sogo Build., 6-1 Marunouchi 2-chome, Chiyoda-ku, Tokyo, 100, Japan.

acetate (VAc) was prepared by using potassium persulfate-SO₂ redox initiator. The copolymer had an intrinsic viscosity of 1.7 ($M_w = 116,000$) in dimethylformamide at 30°C.

Preparation of Fibers

Spinning. Spinning solutions were made by dissolving the above polymers in trifluoroacetic acid. The solutions were transparent and stable at room temperature. The spinning solutions were spun by a dry-spinning process. The spinning conditions are summarized in Table I.

Drawing and Heat Treatment. Undrawn fibers were extracted with boiling methanol for 30 min to remove the solvent retained in the fiber, then dried for 4 hr at 70°C under reduced pressure of 20 mm Hg. The fibers were

TABLE I
Dry Spinning from Trifluoroacetic Acid Solution

	Poly(AN-VAc) ^a	PMAN
Spinning solution		
Concentration, wt-%	12.5	15.5
Temperature, °C	30	30
Nozzle diameter, mm	0.413	0.311
Output, ml/min	0.18	0.17
Spinning cell temperature, °C		
Top	69-72	72-76
Bottom	99-101	92-100
Take-up speed, m/min	9.1	9.0
Draft, times	6.8	4.6
CF ₃ COOH contents in undrawn fiber		
After drying, ^b wt-%	9.32	12.9
After extraction, ^c wt-%	0	0
Denier		
After drying, ^b den.	44	46
After extraction, ^c den.	40	42

^a Copolymer of acrylonitrile and vinyl acetate.

^b At 70°C under vacuum (20 mm Hg) for 10 hr.

^c With boiling methanol for 30 min.

TABLE II
Drawing^a and Heat Treatment for Evaluation of Fiber Properties

Sample no.	Polymer	Draw ratio ^b	Condition of heat treatment
PO-1	PMAN	8.3	in air at 180°C for 15 sec
PO-2	PMAN	11.7	under constant length, and
PO-3	PMAN	13.2	then in boiling water for 30 min under free tension
V-1	poly(AN-VAc)	1.0	in air at 220°C for 15 sec
V-2	poly(AN-VAc)	3.3	under constant length, and
V-3	poly(AN-VAc)	5.8	then in boiling water for
V-4	poly(AN-VAc)	7.5	30 min under free tension

^a Undrawn fibers had previously been extracted with boiling methanol for 30 min and dried for 4 hr at 70°C under vacuum.

^b Drawn at 160°C in air.

then stretched various times their original length at 160°C in air. Samples obtained are summarized in Table II.

RESULTS AND DISCUSSION

Infrared Spectral Examinations of Fibers

Figure 1, curve A, shows the infrared spectrum for the undrawn fiber of PMAN after being dried for 10 hr at 70°C under reduced pressure of 20 mm Hg. The spectrum shows that the fiber contains an appreciable amount of trifluoroacetic acid (see peaks 1780 cm^{-1} , 1170 cm^{-1}) which was estimated to be 12.90% by infrared spectrometry. The trifluoroacetic acid retained in the fiber could be easily removed by the extraction with boiling methanol for 30 min (Fig. 1, curve B).

Figure 2 shows the infrared spectra for the undrawn fiber made from the copoly(AN-VAc) before and after extraction with methanol. The amount of

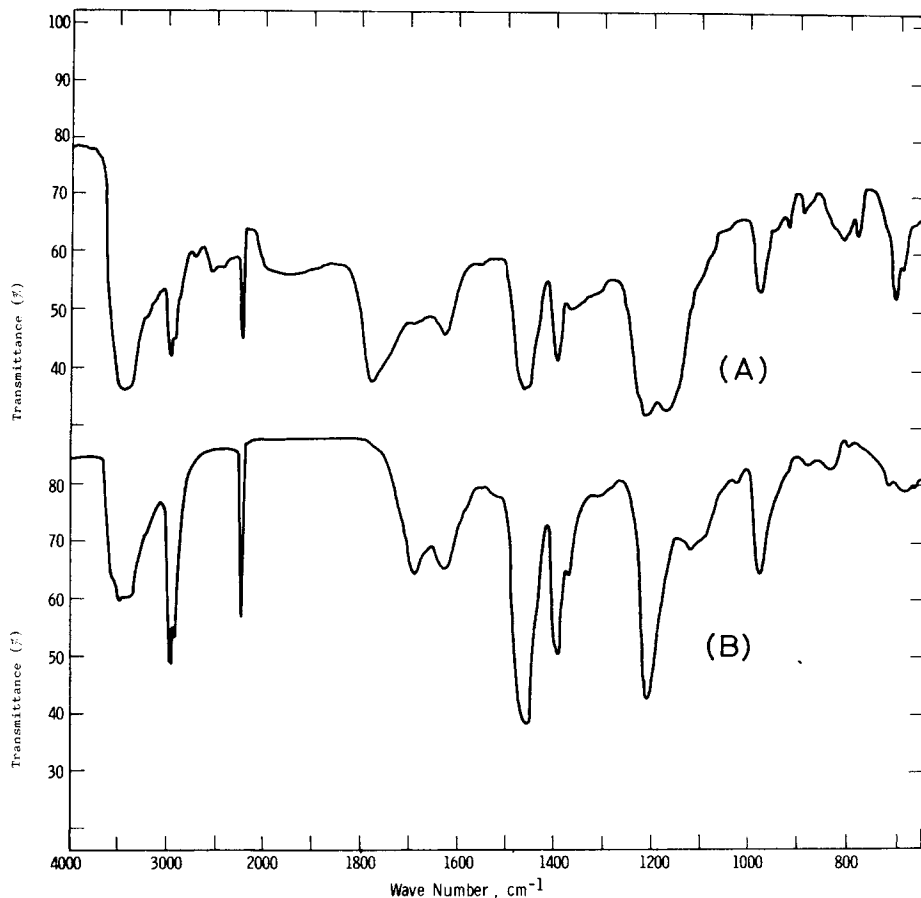


Fig. 1. Infrared spectra for undrawn fiber of PMAN after being dried for 10 hr at 70°C under 20 mm Hg (A) and for the undrawn fiber of PMAN after being extracted with a boiling methanol for 30 min (B).

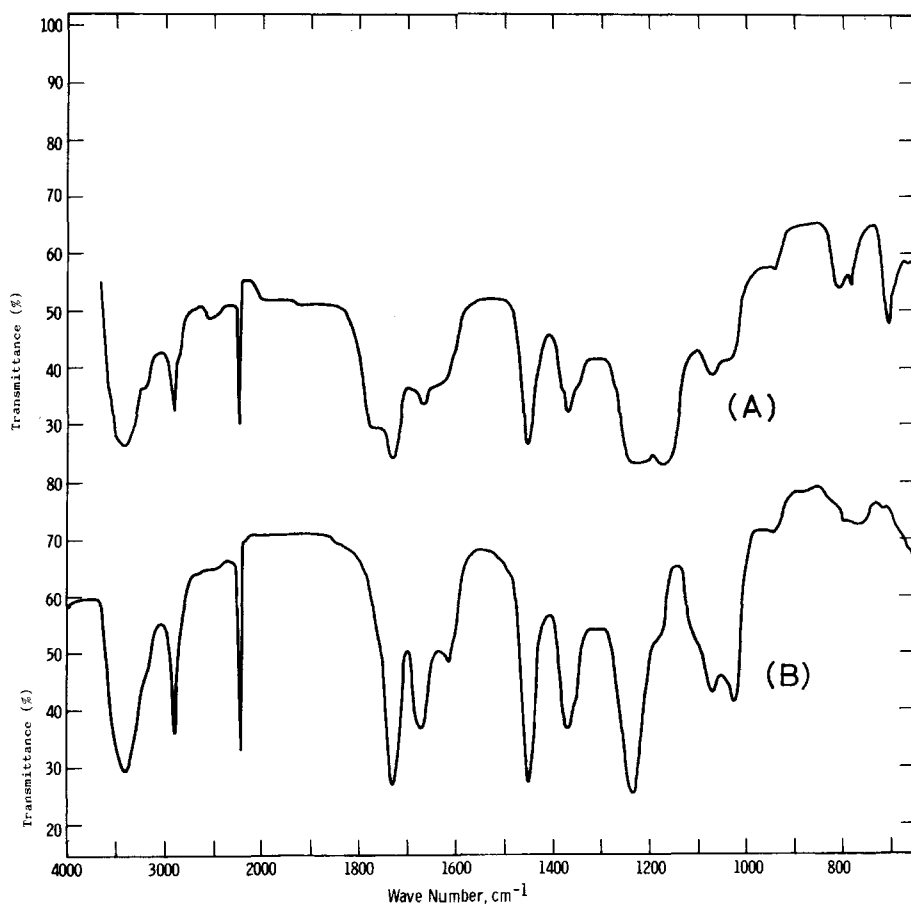


Fig. 2. Infrared spectra for the undrawn fiber made from copoly(AN-VAc) after being dried for 10 hr at 70°C under 20 mm Hg (A) and for the undrawn fiber from copoly(AN-VAc) after being extracted with a boiling methanol for 30 min (B).

trifluoroacetic acid retained in the fiber before extraction was estimated to be 9.32% using infrared spectrometry. Figure 2, curve B, indicates that the extraction with boiling methanol for 30 min is enough to remove the solvent.

Stretchability

The stretchabilities of the undrawn PMAN fibers were carefully examined for the purpose of determining their stretching behavior and to find optimum conditions for drawing.

Figure 3 shows the draw ratios at breakage as a function of temperature for the undrawn PMAN fiber immediately after spinning. An optimum condition for stretching was found to be around 130°C. The optimum temperature did not change after the fibers had been dried for 10 hr at 70°C (Fig. 4). However, maximum draw ratios increased from 4.5–7.0 (before drying) to 5.7–7.8 after drying.

Figure 5 shows the draw ratios at breakage for the undrawn PMAN fiber which has been subjected to extraction with boiling methanol. The optimum

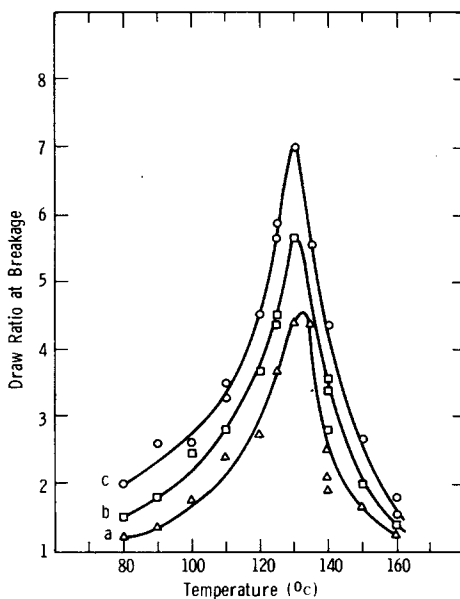


Fig. 3. Draw ratio at breakage as a function of temperature for the undrawn fiber of PMAN immediately after spinning: (a) one breakage in six filaments; (b) three breakages in six filaments; (c) all breakages in six filaments.

temperature for stretching increased to around 160°C. Also, the range of temperature possessing the maximum draw ratio was increased compared with those in Figures 3 and 4. At the same time, maximum draw ratios increased to 7.6–10.5. These results indicate that the optimum temperature

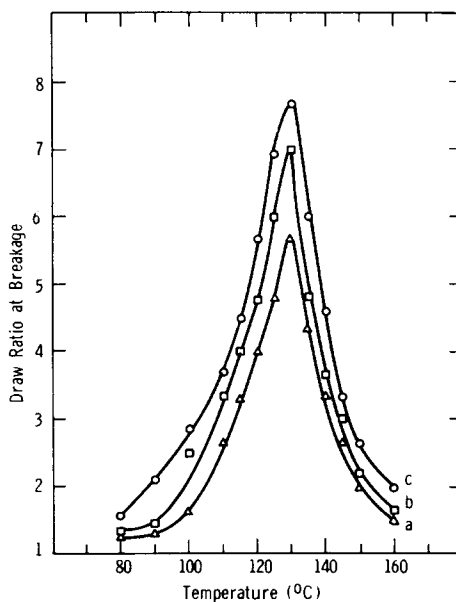


Fig. 4. Draw ratio at breakage as a function of temperature for the undrawn fiber of PMAN previously dried for 10 hr at 70°C under 20 mm Hg: (a) one breakage in six filaments; (b) three breakages in six filaments; (c) all breakages in six filaments.

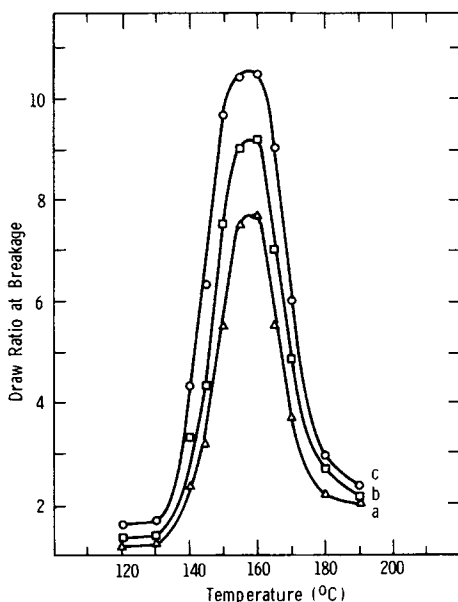


Fig. 5. Draw ratio at breakage for the undrawn fiber of PMAN as a function of temperature. Specimen had previously been extracted with boiling methanol for 30 min and dried for 4 hr at 70°C: (a) one breakage in six filaments; (b) three breakages in six filaments; (c) all breakages in six filaments.

for stretching is greatly influenced by the solvent retained in the fiber which facilitates the mobility of chain molecules.

Figure 6 shows differential thermal analysis (DTA) data for the fibers after being dried (a) and after being extracted with methanol and dried (b). An endothermic peak first appears due to the mobility of polymer chains followed by an exothermic peak due to the crystallization of the polymer, which is one of the characteristic features of crystalline polymers.

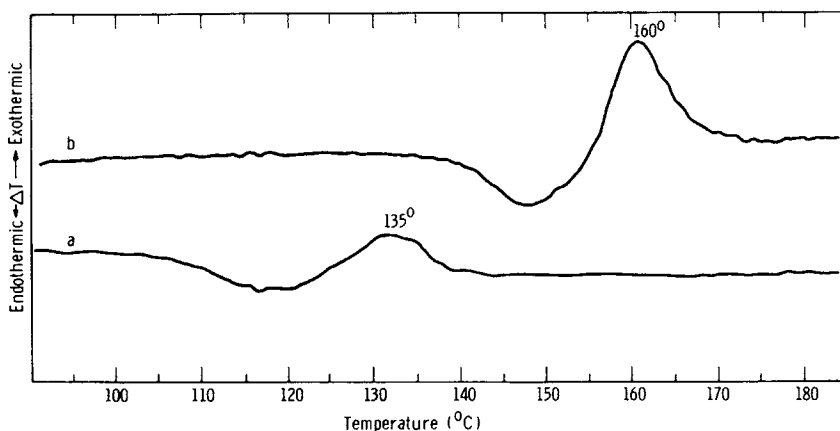


Fig. 6. Differential thermal analyses of undrawn fibers of PMAN on heating. Heating ratio, 10°C/min under 20 mm Hg: (a) dried for 10 hr at 70°C under 20 mm Hg after spinning. Specimen still contained 12.9 wt-% of trifluoroacetic acid. (b) Extracted with boiling methanol for 30 min, then dried for 4 hr at 70°C under 20 mm Hg.

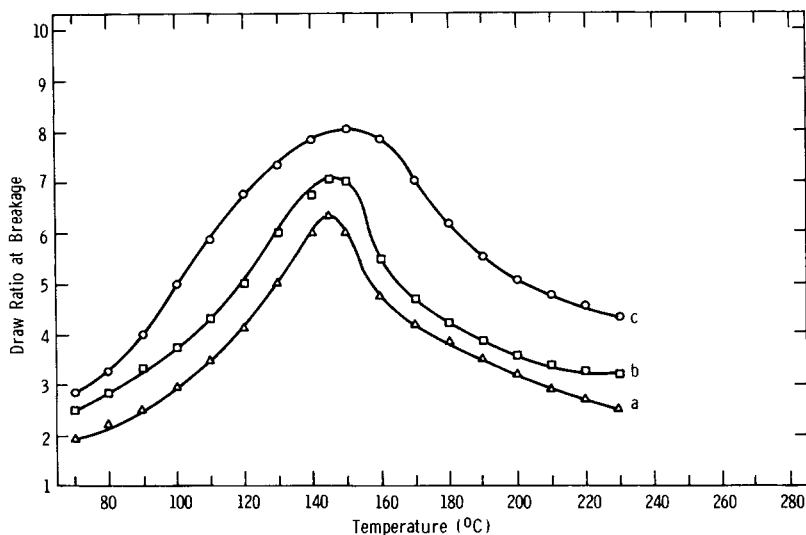


Fig. 7. Draw ratio at breakage as a function of temperature for the undrawn fiber of copoly(AN-VAc) immediately after spinning: (a) one breakage in six filaments; (b) three breakages in six filaments; (c) all breakages in six filaments.

For crystalline polymers, stretchability is generally expected to be optimum at a temperature a little higher than the endothermic peak but a little lower than the exothermic peak so that slow crystallization may occur during stretching. This phenomenon is understandable since mobility of the chains is essential for orientation. At the same time, crystallization to some extent is necessary to provide enough fiber tenacity to permit drawing, but much higher degrees of crystallinity might inhibit chain orientation.

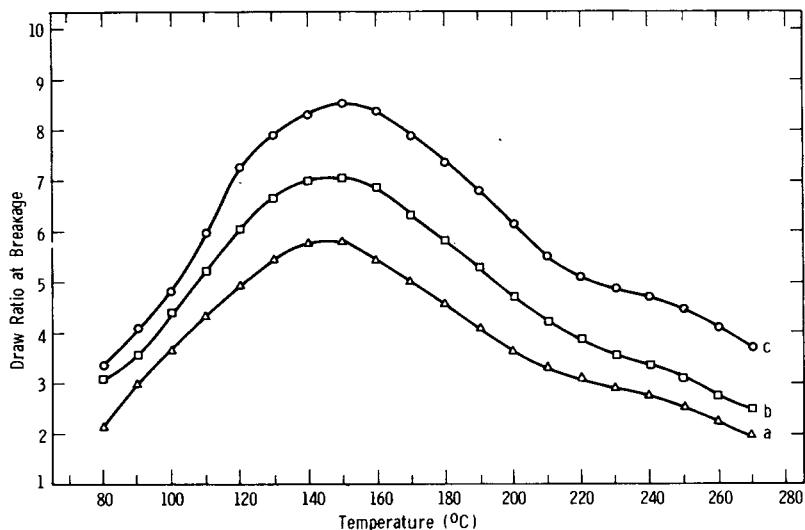


Fig. 8. Draw ratio at breakage as a function of temperature for the undrawn fiber of copoly(AN-VAc) previously dried for 10 hr at 70°C under 20 mm Hg: (a) one breakage in six filaments; (b) three breakages in six filaments; (c) all breakages in six filaments.

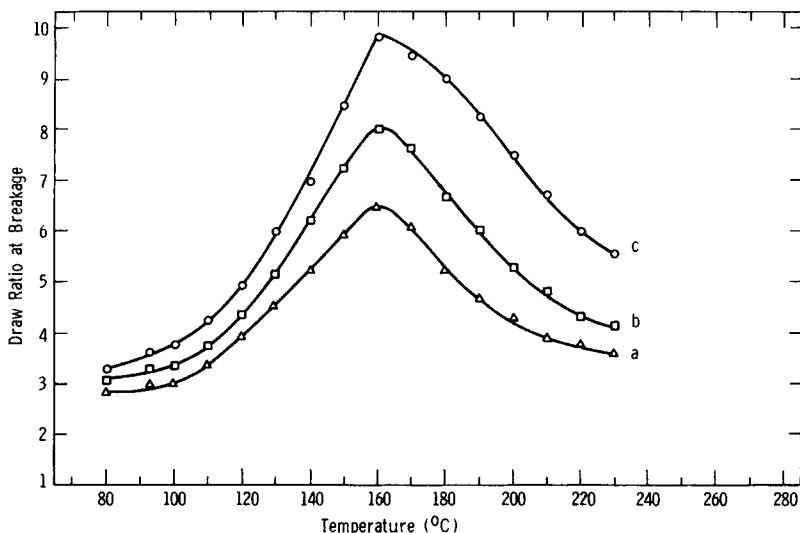


Fig. 9. Draw ratio at breakage for undrawn fiber of copoly(AN-VAc) as a function of temperature. The specimens were previously extracted with boiling methanol for 30 min and dried for 4 hr at 70°C under 20 mm Hg: (a) one breakage in six filaments; (b) three breakages in six filaments; (c) all breakages in six filaments.

The optimum temperatures for stretching shown in Figures 4 and 5 are in good accord with DTA data, that is, the optimum temperature in Figure 4 is about 130°C (5° lower than exothermic peak, 135°C, in curve a in Fig. 6) and that in Figure 5 is about 155°C (5° lower than the peak of curve b in Fig. 6). Thus, the optimum temperatures for stretching are consistent with the DTA data.

In order to compare the stretchability of PMAN fiber with a conventional acrylic fiber, the same set of data were taken using undrawn fibers made from the copoly(AN-VAc). The fibers were prepared in the same process (see Table I). The results are shown in Figures 7-9. The optimum temperature which gave maximum draw ratio was around 150°C for the fibers immediately after spinning (see Fig. 9). Drying did not change the optimum temperature for stretching, probably because the drying condition was insufficient to remove the solvent from the fiber. However, the optimum temperature increased to around 160°C after the extraction of the solvent.

Maximum draw ratio increased in the following order, that is, the fiber immediately after spinning, the fiber after drying, the fiber after extraction of the solvent. This trend is the same as was observed in the case PMAN fiber.

All curves in Figures 7-9 are much broader than those for the PMAN fibers (Figs. 3-5). This means that the allowance of temperature range for stretching is wider for the acrylic fiber, which is a big advantage in a practical operation of stretching. (The fiber was prepared by the conditions shown in Table I, unless otherwise described.)

Heat Setability

In order to know the heat setability of the fibers, the effect of heat treatment on their boil-off shrinkages was examined.

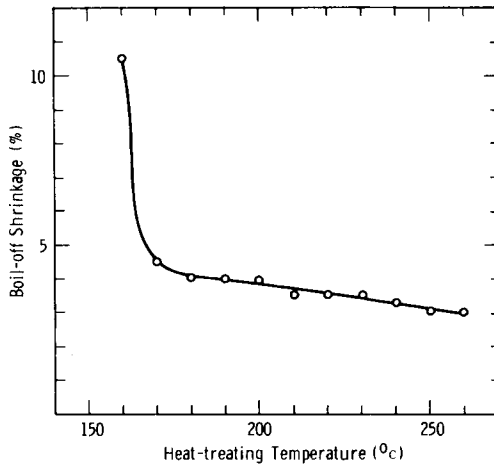


Fig. 10. Effect of heat treatment on boil-off shrinkage for drawn PMAN fiber ($\times 5$ at 160°C after extraction with methanol). Boil-off condition, at 100°C in water for 30 min; heat treatment, in air for 15 sec.

Figure 10 shows the effect of heat treatment on the boil-off shrinkage for the drawn PMAN fiber. The specimens had been stretched five times their original lengths at 160°C and extracted with boiling methanol.

Figure 11 shows the relation between boil-off shrinkage and temperature of

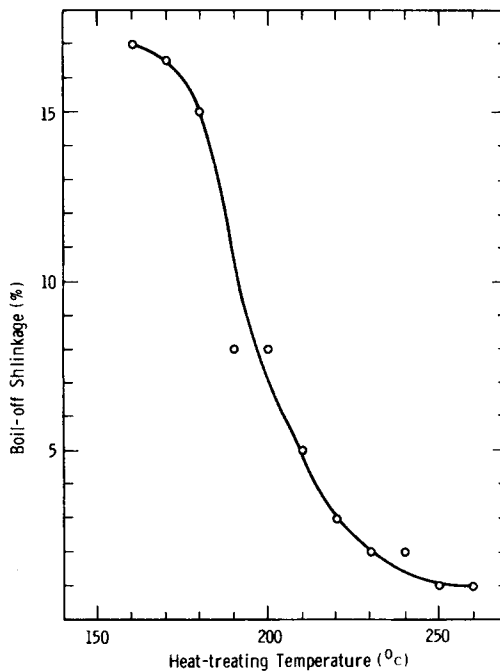


Fig. 11. Effect of heat treatment on boil-off shrinkage for drawn copoly(AN-VAc) fiber (the acrylic fiber) ($\times 5$ at 160°C after extraction with boiling methanol). Boil-off condition, at 100°C in water for 30 min; heat treatment, in air for 15 sec.

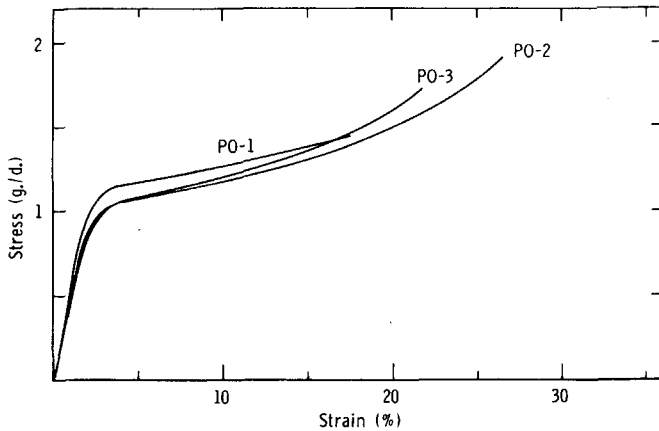


Fig. 12. Stress-strain curve for PMAN fibers at 20°C, 65% R.H. Abbreviations on curves refer to those given in Table II.

heat treatment for the acrylic fiber. The fibers had been stretched and extracted under the same condition as in the case of the PMAN fiber.

These data show that the heat setability of the PMAN fiber is excellent, and the treatment at 190°C is enough to make its shrinkage lower than 4%. However, in the case of the acrylic fiber, heat treatment up to 200°C is still insufficient to make its shrinkage lower than 7%, but treatment at temperatures higher than 220°C enables the attainment of shrinkages lower than those of the PMAN fiber (see Fig. 11).

Mechanical Properties and Resilience of the Fiber

The basic factors controlling fiber properties and resilience are ultimate tensile strength and elongation, tensile modulus, yield point in a stress-strain curve, and compliance ratio.^{14,15} The breaking point (Figs. 12-17) is the ter-

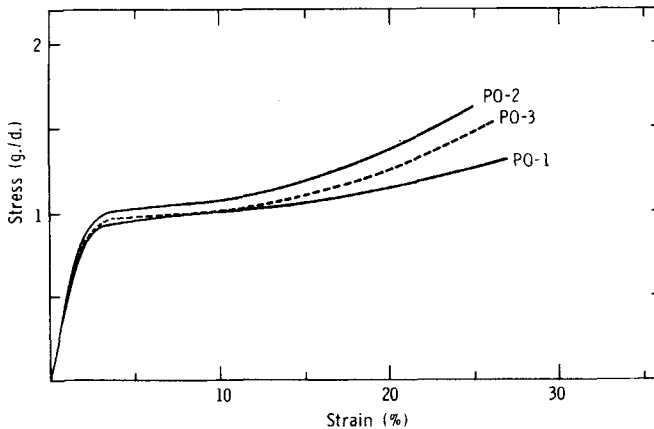


Fig. 13. Stress-strain curves for the PMAN fibers at 20°C in water. Abbreviations on curves refer to those given in Table II.

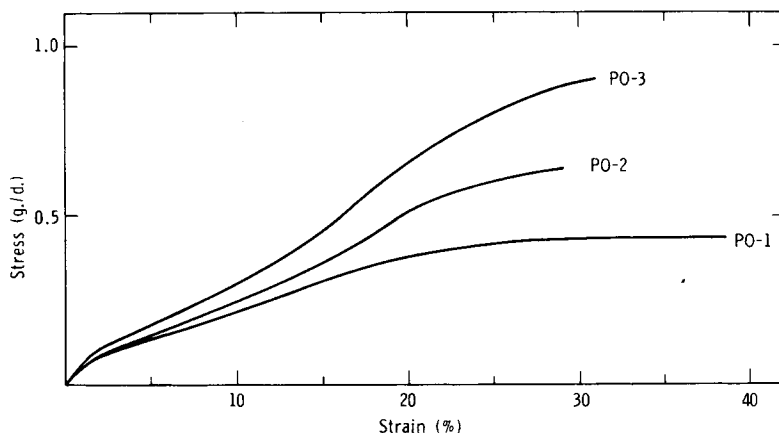


Fig. 14. Stress-strain curves for PMAN fibers at 90°C in water. Abbreviations on curves refer to those given in Table II.

mination of the stress-strain curve, and it is expressed by the ultimate strength and extensibility of the fiber.

Judging from fibers on the market today, the minimum strength a fiber must exhibit is about 1 g per denier.¹⁶ The bulk of synthetic fibers, textile grade, range mostly from 1.5 to 5.0 g/d in strength. Elongation at which the fiber breaks is an important consideration. Elongation is important in several aspects in its own right. First of all, elongation at break must be great enough to allow the fiber to satisfy the fiber strain requirements in fabric or yarn use. A lower limit of about 5% would satisfy these,¹⁶ but most synthetics are well above this elongation. The fibers from PMAN meet all these needs as shown in Figures 12-14 and Table III.

The consideration of recovery of fibers bring us to the second region of importance in the stress-strain curve, the so-called "yield point" or "yield region." The recovery of a fiber from elongations greater than "yield point"

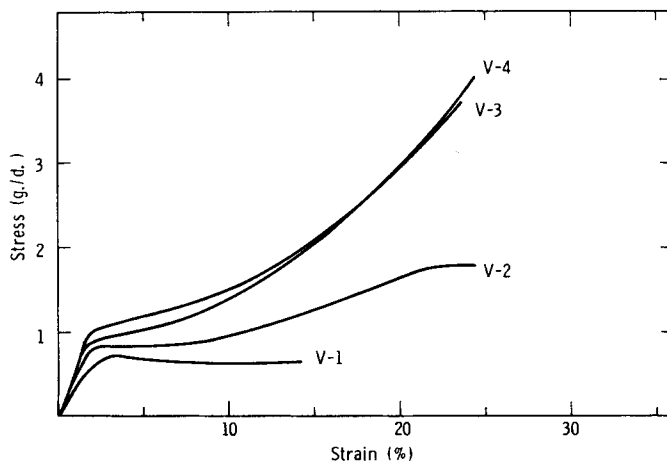


Fig. 15. Stress-strain curves for copoly(AN-VAc) fibers at 20°C, 65% R.H. Abbreviations on curves refer to those given in Table II.

TABLE III
Tensile Properties of PMAN Fiber in Comparison with Copoly(AN-VAc) Fiber

	PO-1	PO-2	PO-3	V-1	V-2	V-3	V-4
Denier	5.04	3.58	3.18	39.1	12.2	6.96	5.36
Specific gravity	1.131	1.121	1.125	1.192	1.192	1.191	1.193
Boil-off shrinkage, %	2.0	4.3	4.3	0	2.5	6.5	8.5
Tensile strength							
Dry, g/d	1.45	1.91	1.72	0.637	1.78	3.73	4.04
Wet, g/d	1.31	1.62	1.53	0.57	1.34	3.02	3.43
90°-wet, g/d	0.463	0.639	0.902	0.069	0.361	1.04	1.75
Retention							
Wet/dry, %	90.3	84.8	88.9	89.5	75.4	81.0	84.8
90°-Wet/dry, %	31.9	33.5	52.4	10.8	20.3	27.9	43.3
Tensile elongation							
Dry, %	17.5	26.5	21.7	14.2	24.4	23.5	24.4
Wet, %	27.0	25.0	26.1	1.97	26.4	25.1	26.4
90°-Wet, %	38.6	29.1	31.0	>400	128	50.1	36.0
Retention							
Wet/dry, %	154	94.3	120	13.9	108	107	108
90°-Wet/dry, %	220	110	143	300	524	213	148
Initial tensile modulus							
Dry, g/d	56.8	52.2	49.1	37.2	48.9	58.9	57.2
Wet, g/d	48.2	54.7	52.0	32.7	47.0	55.1	53.9
90°-Wet, g/d	4.40	5.15	6.07	0.345	0.954	1.32	1.16
Retention							
Wet/dry, %	86.7	105	106	88.0	96.1	93.4	94.3
90°-Wet/dry, %	7.74	9.88	12.4	0.93	1.95	2.24	2.03

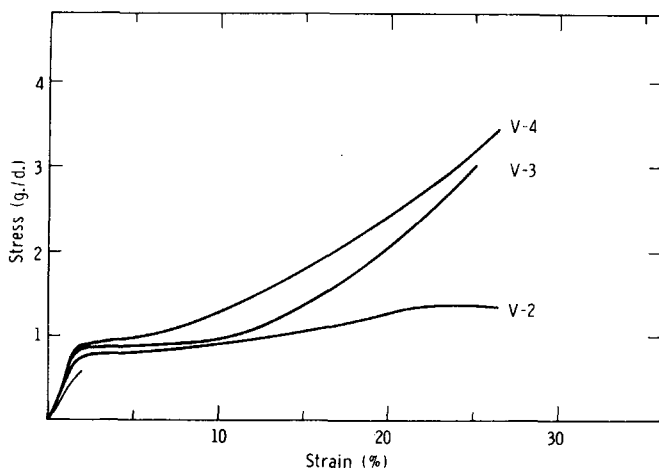


Fig. 16. Stress-strain curves for copoly(AN-VAc) fibers at 20°C in water. Abbreviations on curves refer to those given in Table II.

elongation is relatively poor, while the recovery from elongations lower than the "yield point" is relatively good.

It is this relation between the "yield point" and recovery or resilience of fibers that makes the "yield point" an important region in the stress-strain curve. A "yield point" of about 2% extension generally results in a fiber with very good recovery and fabrics of high resilience.¹⁶ Figures 12 and 13 show that yield points of the PMAN fiber appear at about 2.0% elongation in air (20°C, 65% R.H.) in water (20°C), while the fibers from the copolymers (AN-VAc) show their yield point at about 1.7% elongation. Therefore, the PMAN fiber seems to be promising for practical use. When it comes to the behavior under hot-wet condition, the PMAN fiber still shows a clear yield point at about 1.4–1.8% elongation (see Fig. 14), while the acrylic fiber shows no yield point (Fig. 17). This reflects the fact that the acrylic fibers have very poor hot-wet properties which result in big changes in "hand" and "hand feeling"

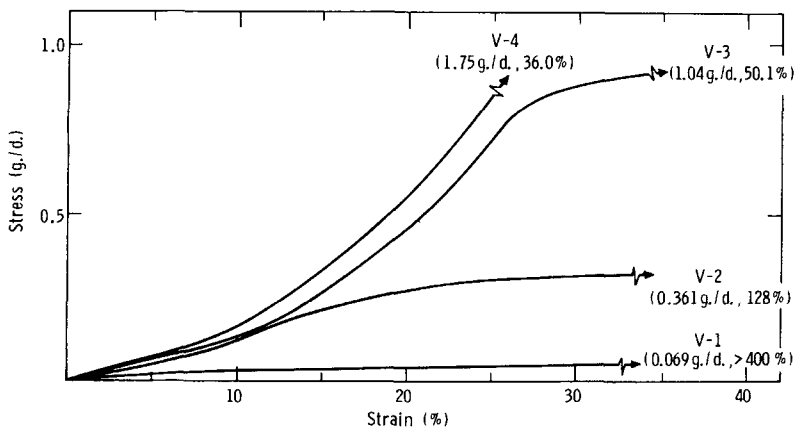


Fig. 17. Stress-strain curves for copoly(AN-VAc) fibers at 90°C in water. Abbreviations on curves refer to those given in Table II.

of their products after dyeing or washing. From the facts mentioned above, the PMAN fiber is expected to have a better "hot-wet property" than conventional acrylic fibers.

Compliance Ratio and Resilience Map

The usefulness of the "compliance ratio" (CR) was proposed by Hoffman et al.^{14,15} on the basis of the fact that in the case of fabric hand, the significance of curves in stress-strain relation persists to the range between 5% and 10% elongation. The compliance ratio was developed in stiffness in that region of extension or strain and is given in the following mathematical terms:

$CR \equiv (\text{compliance at 10\% elongation} - \text{compliance at 5\% elongation})/5$

$$\equiv \frac{10/L_{10} - 5/L_5}{5}$$

$$\equiv \frac{2}{L_{10}} - \frac{1}{L_5}$$

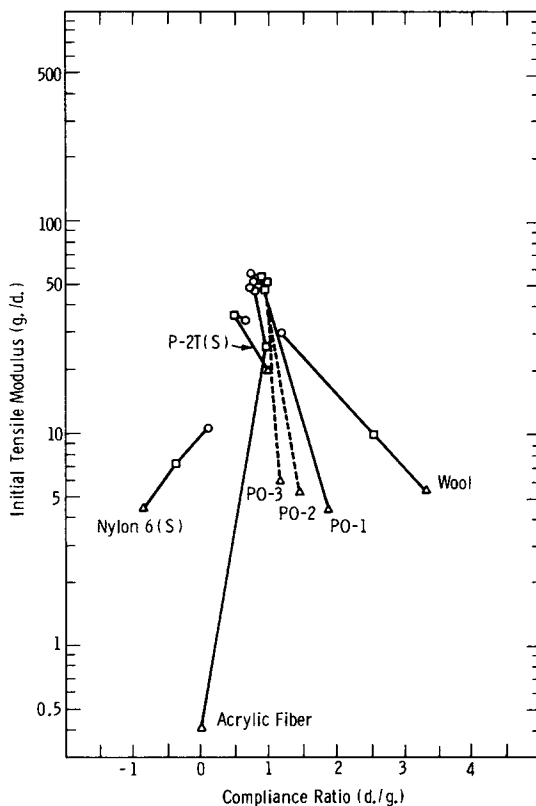


Fig. 18. Resilience map for the PMAN fiber at 20°C, 65% R.H. (○), 20°C in water (□), and 90°C in water (Δ). PO-1, PO-2, PO-3 refer to those given in Table II. P-2T means poly(ethylene terephthalate); (S) means staple fiber.

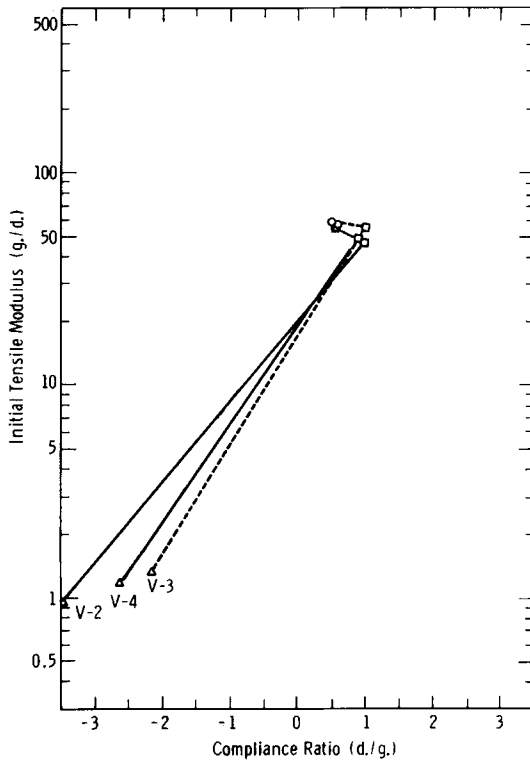


Fig. 19. Resiliency map for the copoly(AN-VAc) fiber at 20°C, 65% R.H. (O), 20°C in water (□) and 90°C in water (Δ). Abbreviations are those given in Table II.

where L_{10} and L_5 are the stresses in grams per denier at 10% and 5% elongation, respectively. The correlation between tensile modulus and compliance ratio is very useful in defining types of resilience, for example, wool is characterized by a relatively low modulus and high compliance ratio, silk by high stiffness and low compliance ratio, and nylon represents a third combination—low stiffness and low compliance ratio.

It is very significant to compare the changes in position in the resilience map between the PMAN fiber and the acrylic fiber with those of wool.

The changes in position for the PMAN fiber in air (20°C, 65% R.H.), in water (20°C), and in water (90°C) are similar to the changes for wool, although the magnitude of change from air to water (20°C) for the PMAN fiber is very small (Fig. 18).

It is very interesting to compare these changes in position with those of the acrylic fiber. The poor hot-wet property of the acrylic fiber is well understood by a change in position in the maps at hot-wet condition (Figs. 18 and 19). From the above fact it may be said that the PMAN fiber is a more wool-like fiber than the acrylic fiber.

In Table III, the mechanical properties of the PMAN fiber are summarized in comparison with those of the acrylic fiber produced in the same dry spinning. The mechanical properties shown in this table are well acceptable for practical use.

From the data in Table III, it can be said that compared to the acrylic fiber, the PMAN fiber has good tensile properties. Strain (%) at yield point for the PMAN fiber is higher than that of the acrylic fiber, and also the PMAN fiber shows higher elastic recovery than the acrylic fiber. Along with the data of compliance ratio (Table III and Fig. 18), the fibers from the crystalline polymethacrylonitrile is expected to be one of the most promising fibers having wool-like properties.

Grateful acknowledgment is made to the continued encouragement of Drs. T. Isoshima and T. Tomita. Thanks are also due to Drs. N. Yamada, T. Yoshihara, and S. Minami for their helpful discussions and also to the Mitsubishi Rayon Co. for permission of this publication.

References

1. G. Natta and G. Dall'Asta, *Chim. Ind. (Milan)*, **46**, 1429 (1964).
2. Y. Joh, T. Yoshihara, Y. Kotake, F. Ide, and K. Nakatsuka, *J. Polym. Sci. B*, **3**, 933 (1965).
3. Y. Joh, T. Yoshihara, Y. Kotake, F. Ide, and K. Nakatsuka, *J. Polym. Sci., B*, **4**, 673 (1966).
4. Y. Kotake, T. Yoshihara, H. Sato, N. Yamada, and Y. Joh, *J. Polym. Sci., B*, **5**, 163 (1967).
5. T. Yoshihara, Y. Kotake, and Y. Joh, *J. Polym. Sci., B*, **5**, 459 (1967).
6. Y. Joh, Y. Kotake, T. Yoshihara, F. Ide, and K. Nakatsuka, *J. Polym. Sci. A-1*, **5**, 593 (1967).
7. Y. Joh, Y. Kotake, T. Yoshihara, F. Ide, and K. Nakatsuka, *J. Polym. Sci. A-1*, **5**, 605 (1967).
8. Y. Joh, T. Yoshihara, Y. Kotake, Y. Imai, and S. Kurihara, *J. Polym. Sci. A-1*, **5**, 2503 (1967).
9. Y. Joh, T. Yoshihara, S. Kurihara, I. Tsukuma, and Y. Imai, *Macromol. Chem.*, **119**, 239 (1968).
10. Y. Joh, S. Kurihara, T. Sakurai, Y. Imai, T. Yoshihara, and T. Tomita, *J. Polym. Sci. A-1*, **8**, 377 (1970).
11. Y. Joh, T. Yoshihara, S. Kurihara, T. Sakurai, and T. Tomita, *J. Polym. Sci. A-1*, **8**, 1901 (1970).
12. Y. Joh, S. Kurihara, T. Sakurai, and Y. Tomita, *J. Polym. Sci. A-1*, **8**, 2383 (1970).
13. Y. Joh, S. Kurihara, and T. Tomita, *J. Polym. Sci. A-1*, **9**, 1463 (1972).
14. L. F. Beste, and R. M. Hoffman, *Text. Res. J.*, **20**, 441 (1950).
15. R. M. Hoffman and L. F. Beste, *Text. Res. J.*, **21**, 66 (1951).
16. R. M. Hoffman, *Text. Res. J.*, **18**, 141 (1948).

Received June 26, 1974

Revised June 19, 1975